LANGLEY GRANT

7N-25-CR

AIAA

NAG1-416

A COMPARATIVE μSR STUDY OF TITANIUM AND YTTRIUM DIHYDRIDES.

114140

W. J. KOSSLER*, H. E. SCHONE*, J. R. KEMPTON*, B. HITTI*, C. E. STRONACH**, G. A. STYLES***, E. F. W. SEYMOUR***.

p.17

*Physics Department, College of William and Mary, Williamsburg, VA 23185 USA.

**Physics Department, Virginia State University, Petersburg, VA 23803 USA.

***Physics Department, University of Warwick, Coventry CV4 7AL England.

Summary

Transverse depolarization data have been obtained at the AGS facility at Brookhaven National Laboratory, in a magnetic field of 150 G and over a temperature range 10K<T<600K, for powder samples of $TiH_{1.99}$, $TiH_{1.97}$, $TiH_{1.83}$, and $YH_{2.00}$.

As a function of temperature all samples show two plateaus in depolarization rate Λ, followed at higher temperatures by a continuous decrease in Λ. Below a temperature which differs according to hydrogen concentration (e.g. ≈ 270 K for $TiH_{1.97}$), Λ takes a temperature-independent value which decreases as hydrogen content decreases. This is interpreted as indicating that at high hydrogen concentrations muons mainly occupy octahedral(O) sites, being unable to reach a vacant, preferred, tetrahedral(T) site on the hydrogen sublattice. The fraction which is successful in

(NASA-CR-181600) A COMPARATIVE MUON SPIN ROTATION STUDY OF TITANIUM AND YTTRIUM DIHYDRIDES (College of William and Mary) 17 p

N88-70100

Unclas

00/25 0114140

locating a T site vacancy increases with decreasing hydrogen content thus accounting for the observed decrease in Λ. The data for TiH_x are consistent with O site occupation by hydrogen equal to zero.

The decrease in Λ to a new temperature-independent value which occurs at temperatures where the protons are still essentially static is attributed to increased muon mobility; the muons escape from the O sites and become trapped at vacant T sites. The results for $YH_{2.00}$ are quantitatively different from those for TiH_x even after allowance is made for the difference in lattice constants. The lower plateau value is consistent with predominant T site occupation by hydrogen but with partial O site occupation in conformity with previous NMR and neutron scattering data for yttrium dihydride.

The high-temperature decrease in Λ occurs in the same temperature range as the diffusional narrowing of the proton NMR absorption line. The best fits to the muon data give activation energies smaller than for proton diffusion even though at high hydrogen concentrations both proton and muon diffusion must be controlled by tetrahedral lattice vacancies.

Introduction

In order to understand the microscopic features of the distribution and diffusion of light interstitial particles in metals, it is desirable to use a variety of techniques which might include neutron scattering, NMR of hydrogen, deuterium, and metal nuclei, and μ^+SR in which one can regard the positive muon as a light isotope of hydrogen.

In this paper we report on μSR experiments on non-stoichiometric titanium and yttrium dihydrides which have similar structures: the metal atoms in each case form a FCC lattice and the hydrogen ions occupy interstitial sites which are known to be the tetrahedral(T) sites (forming a simple cubic lattice with lattice parameter half that of the metal lattice, Figure 1) in $TiH_{\approx 2}$; and a similar structure occurs for $YH_{\approx 2}$ except that it is believed that a small proportion of the octahedral(O) interstitial sites(forming a FCC lattice identical with the metal lattice) are occupied by hydrogen ions at the expense of a fraction of the preferred T sites[1,2]. One of the objects of the present experiments was to search for differences between μSR characteristics for the two systems which might reflect and quantify the extent of O site occupation.

The basic experiment proceeds by examining the muon depolarization rate. It is convenient to make these measurements in a modest transverse magnetic field and to observe the time dependence of the muon decay signal produced by the resulting precession. It can also be helpful in investigating the onset of muon diffusional motion to make measurements in zero magnetic field. At low temperatures where the muons and hydrogen nuclei are both stationary the muon samples local dipolar fields of the protons (in the present cases the metal nuclei do not contribute appreciably to the dipolar field) and the consequent dephasing rate is a sensitive measure of the dipolar fields and hence of the sites occupied by the muons and, simultaneously, of the disposition of protons around them. At higher temperatures both muons and protons can diffuse and the observed depolarization rates then reflect the time-average dipolar field (in a manner analogous to motional averaging in NMR) and hence yield information on the diffusional motions of both species.

2. Experimental

The samples consisted of metal powders hydrided to various γ-phase(FCC) compositions directly from the gas phase. The sample thickness was of order 2.5 g cm^{-2} to provide adequate muon stopping power, and samples were contained in evacuated aluminum cells provided with mylar windows. The purity was such that the chance of trapping of muons by residual impurities could be neglected. Indeed no trapping of muons by point and other defects was anticipated (or found) since such traps would already be saturated by hydrogen ions. The particle size was 75-150 μm which was sufficiently large that no complications due to diffusion to, and depolarization at, particle surfaces need be considered. The samples investigated were of compositions $TiH_{1.99}$, $TiH_{1.97}$, $TiH_{1.83}$, and $YH_{2.00}$.

Magnetic fields of 150 G were provided by Helmholtz coils providing a precession rate in the transverse mode of about 2 MHz. A temperature range $10K<T<600K$ was attained by use of a helium closed-cycle refrigerator and a conventional furnace. The muon beam and attendant experimental facilities will be described elsewhere[3].

3. Results

The depolarization rates observed in a transverse field were represented for all samples by a function $\exp(-\Lambda^2t^2)$. At low temperatures at which muon motion does not occur $\exp(-\Lambda^2t^2) = \exp(-\sigma^2t^2/2)$ where σ^2 is the second moment of the frequency distribution due to the dipolar fields. At high temperatures, for the purpose of extracting diffusion information, the more general function

$$\exp\{-\sigma^2\tau^2[\ \exp(-t/\tau) - 1 + t/\tau]\}$$

was used to take account of random time fluctuations of the dipolar field experienced by the muons, due to muon and/or proton motions, with correlation time τ. This formula was used to analyze the higher temperature data where a Gaussian shape function would not be expected to hold. The experimental results for $\Lambda(T)$ as a function of temperature are shown in Figures 2 and 3.

Zero field measurements were made for $YH_{2.00}$ at 20K and 295K. The curve at 20K shows some recovery of the dephasing function $G(t)$ towards $(1/3)G(0)$ after passing through a minimum, though without ever reaching the value $(1/3)G(0)$, which is the asymptotic value for a stationary muon; this is consistent with there being only very slow diffusional motion of the muons at this temperature as indicated by the transverse field data. The curve at 295K shows no recovery following the initial decay, again confirming that considerable muon motion is occurring ($\sigma\tau$<3).

4. Discussion

We first discuss the low temperature results for the Ti-H system. As a function of temperature all samples show two plateaus in depolarization rate Λ followed at high temperatures by a continuous decrease in Λ. Below a sample-dependent temperature, Λ takes a temperature-independent value which increases as the hydrogen concentration increases. This is shown in Figure 4 where the square of this value of Λ is plotted as a function of fractional vacancy concentration on the T sub-lattice, (2-x)/2. The data can thus be represented by a linear relation. This significant result is interpreted as indicating that at high hydrogen concentrations muons come to rest in O sites and remain there except in those instances where one of the 8 nearest neighbor T sites happens to be vacant. Under these circumstances the observed average depolarization rate is a weighted mean:

$$\Lambda_{exp}^2 = \Lambda_O^2(1-(8(2-x)/2)) + \Lambda_T^2(8(2-x)/2) \qquad (1)$$

where the values Λ_O and Λ_T are the rates characteristic of O and T sites, respectively, arising from the dipolar interactions with surrounding protons. The straight line is calculated from equation (1); the value of Λ_T for best fit to the data coincides with the higher temperature plateau value common to $TiH_{1.97}$ and $TiH_{1.83}$. The significance of this will be discussed below.

In calculating Λ_O and Λ_T it is necessary in principle to allow for the mutual spin-flip rate of the protons which reduces the fourth moment of the muon signal without affecting the second moment. This has the effect of narrowing the observable part of the signal [5] and changing the shape from a Gaussian to some extent. We estimate that here the fourth moment is reduced by 23% compared with a situation in which the proton spin orientations are frozen; the deviation of the line shape from Gaussian is not large and is indeed undetectable, and the observed linewidth is decreased by approximately 5%. The resulting calculated value of Λ_O is 0.298 μs^{-1} compared with the experimentally fitted value of (0.252 ± 0.004) μs^{-1}. The small difference is plausibly accounted for by a local displacement of nearest neighbor protons away from the muon by 0.1 Å.

Our interpretation of the lower plateaus observed at higher temperature is that here the muon is sufficiently mobile that it is able to locate a vacancy on the T lattice. The new values of Λ_T (0.189 μs^{-1} calculated; (0.172 ± 0.005) μs^{-1} fitted) for TiH_x are consistent with this interpretation if we postulate a small (≈ .07 Å) local expansion around the muon, or alternatively take the muon wave function to be spread out around the T site, with a small probability density on the four neighboring O sites.

The low temperature results for $YH_{2.00}$ are quantitatively different from that for TiH_x even when allowance is made for the difference in lattice constants. At the lowest temperature Λ increases to a value appropriate to a situation in which all T sites are filled by protons (there are 2 T sites per metal atom) and all muons must therefore reside on O sites. The upper horizontal line in Figure 3 represents Λ_O and passes through the low temperature limiting value of the data.

As soon as the temperature begins to increase, however, Λ decreases. This is simply explained if a proportion of protons relax from their T sites to nearest O sites; this process does not require that protons should be capable of diffusional motion at this low temperature, of course. The vacated T sites are then available for muon occupation. The plateau value reached shows that, according to equation (1), (4.2 ± 1.5)% of O sites are occupied. This result is to be compared with the value obtained from NMR[1] of (15 ± 3)% at 180K, and that obtained from neutron-diffraction[2] of (12 ± 6)% at 11K and (13 ± 3)% at 300K. Our value is temperature independent between ≈100K and ≈300K. This fraction is not expected to change appreciably with temperature[5] since the effect of the normal Boltzmann factor is thought to be counteracted by large amplitude hydrogen vibrations at high temperature which inhibit occupation of nearest neighbor T and O sites.

At higher temperatures($T>360K$) when all the muons are capable of searching out vacant T sites a further small reduction in Λ occurs as expected. The lower horizontal line through the value of Λ_T in Figure 3 is obtained by simple scaling from the TiH_2 case.

The highest temperature decrease in Λ for all samples occurs in the temperature ranges in which motional narrowing of the proton NMR absorption lines takes place [6,7], and is clearly associated with proton diffusional motion. Since the muon can only move when a proton (or a vacancy) moves, one might expect that both τ_0 and E_a characterizing the muon motion ($\tau = \tau_0 \exp(E_a/kT)$) would be identical with that deduced for protons from NMR relaxation data. Although the absolute values of τ for TiH_x (figure 5) are indeed similar for muons and protons, the values of E_a are quite distinctly smaller for muons than protons; 0.38 ± 0.02 eV for TiH_x for muons compared with 0.505 eV for protons[7]. For $YH_{2.00}$ we obtain 0.4 ± 0.1 eV for muons compared with 0.435 eV for protons[8]; the uncertainty is large enough that it is not clear whether a real difference exists for $YH_{2.00}$. We believe that the results for TiH_x indicate significant muon-proton interactions as discussed for NbH_x by Richter et al[9]. A detailed discussion of this point will be presented elsewhere[10].

5. Conclusion

There is a significant difference in site occupation by hydrogen in γ-TiH_x and γ-YH_x. In the former the hydrogen occupies solely tetrahedral sites, whereas in the latter at $x = 2.0$ approximately 4 % of hydrogen ions occupy octahedral sites, except at the lowest temperatures ($T < 50K$).

The activation energy for muon diffusion for the Ti-H system is considerably lower than that deduced for protons from NMR studies. This is attributed to muon-proton interactions. Similar considerations may apply to $YH_{2.00}$ but a firm conclusion must await the results of measurements at higher temperatures for this system, which are currently in progress.

Acknowledgements

This work was supported by the NSF (grant DMR 8503223), NASA (grant NAG-1-416), and the UK SERC. We are grateful to J. J. Reilly for provision of two titanium hydride specimens and for analysis of samples.

Figure 1. The fluorite structure of γ-TiH_2 and γ-YH_2 phases. The squares represent metal atoms, solid circles tetrahedral hydrogen sites, and open circles octahedral sites.

Figure 2. Depolarization rates for titanium dihydride samples as a function of temperature. The lines are included as a guide to the eye.

Figure 3. Depolarization rate for yttrium dihydride as a function of temperature. The upper and lower horizontal lines indicate Λ_O and Λ_T, respectively.

Figure 4. The low-temperature value of Λ^2 for TiH_x samples as a function of vacancy concentration (2-x)/2.

Figure 5. Diffusional correlation times for muons and protons deduced from the motional decrease of Λ and the NMR motional narrowing [7], respectively, as a function of reciprocal temperature.

References

1. D. L. Anderson, R. G. Barnes, D. T. Peterson, and D. R. Torgeson, Phys. Rev. B21 (1980) 2625.

2. D. Khatamian, W. A. Kamitakahara, R. G. Barnes, and D. T. Peterson, Phys. Rev. B21 (1980) 2622.

3. W. J. Kossler, to be published.

4. A. Abragam, Principles of Nuclear Magnetism (Oxford, Clarendon Press) 1962.

5. P. M. Richards, J. Solid State Chem. 43 (1982) 5.

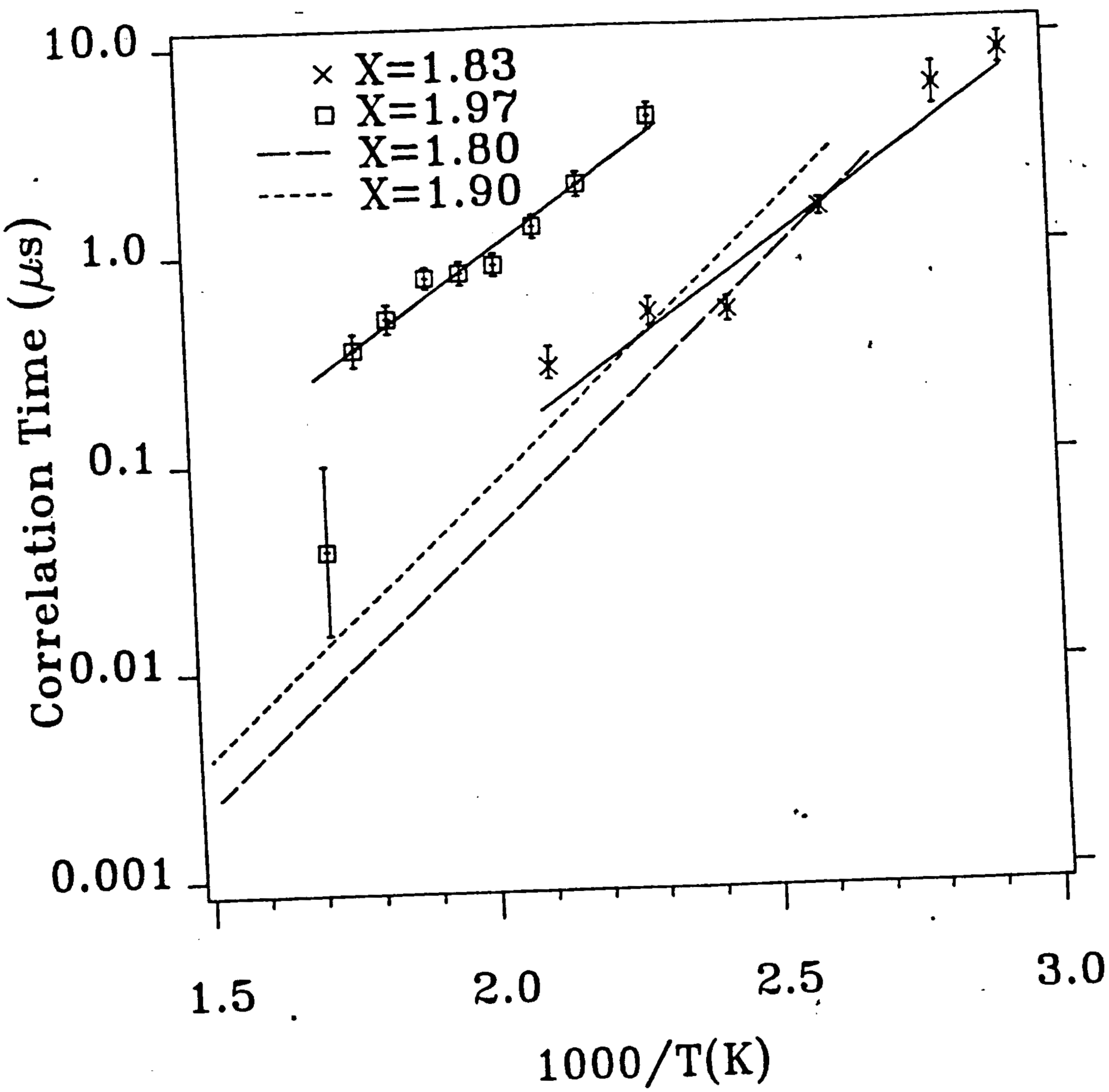
6. D. L. Anderson, M.S. Thesis, Iowa State University, 1979 (unpublished).

7. C. Korn and D. Zamir, J. Phys. Chem. Solids 31 (1970) 489.

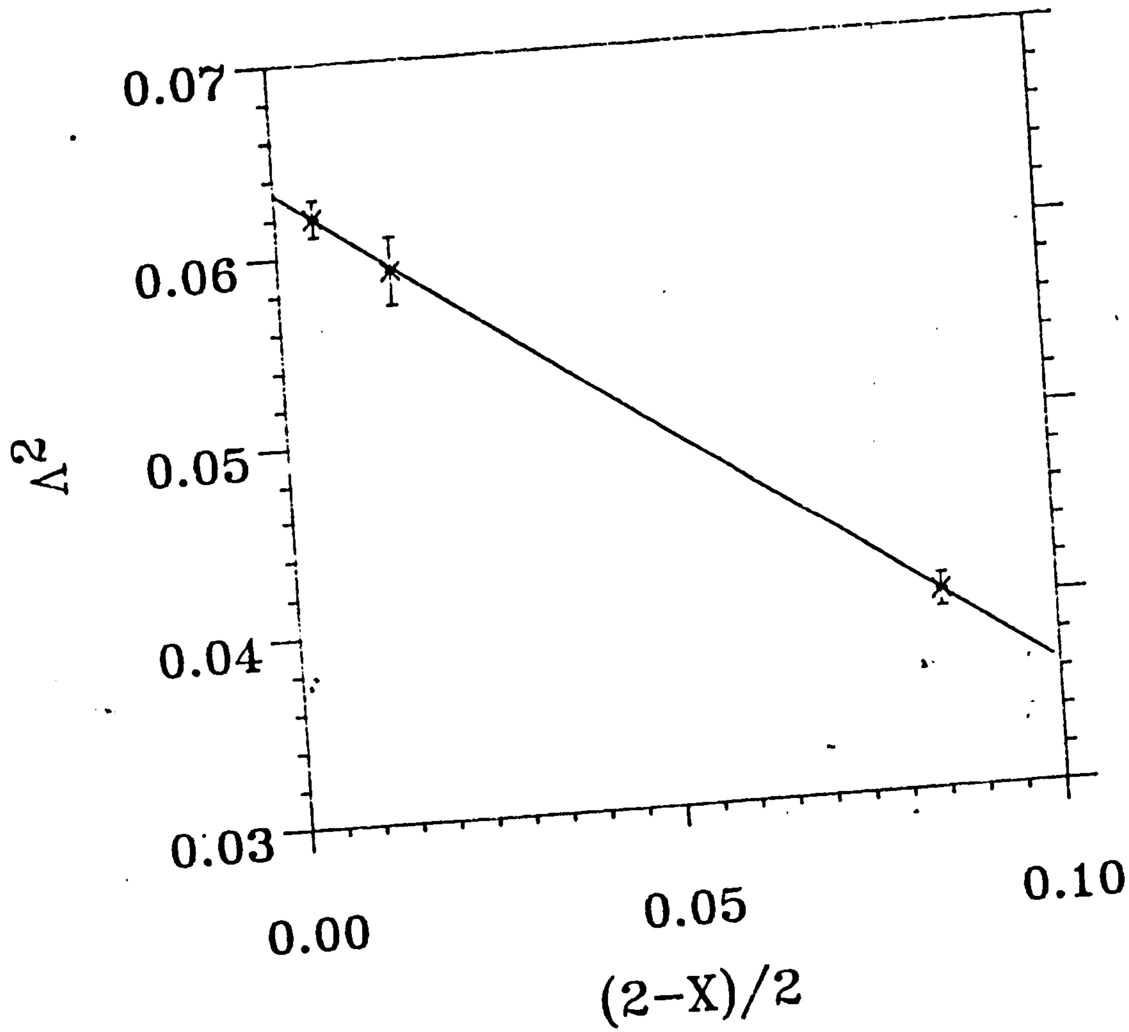
8. T. T. Phua, B. J. Beaudry, D. T. Peterson, D. R. Torgeson, R. G. Barnes, M. Belhoul, G. A. Styles, and E. F. W. Seymour, Phys. Rev. B28 (1983) 6227.

9. D. Richter, R. Hempelmann, K. W. Kehr, O. Hartmann, E. Karlsson, L. O. Norlin, and S. F. J. Cox, Hyperfine Interactions 17-19 (1984) 261.

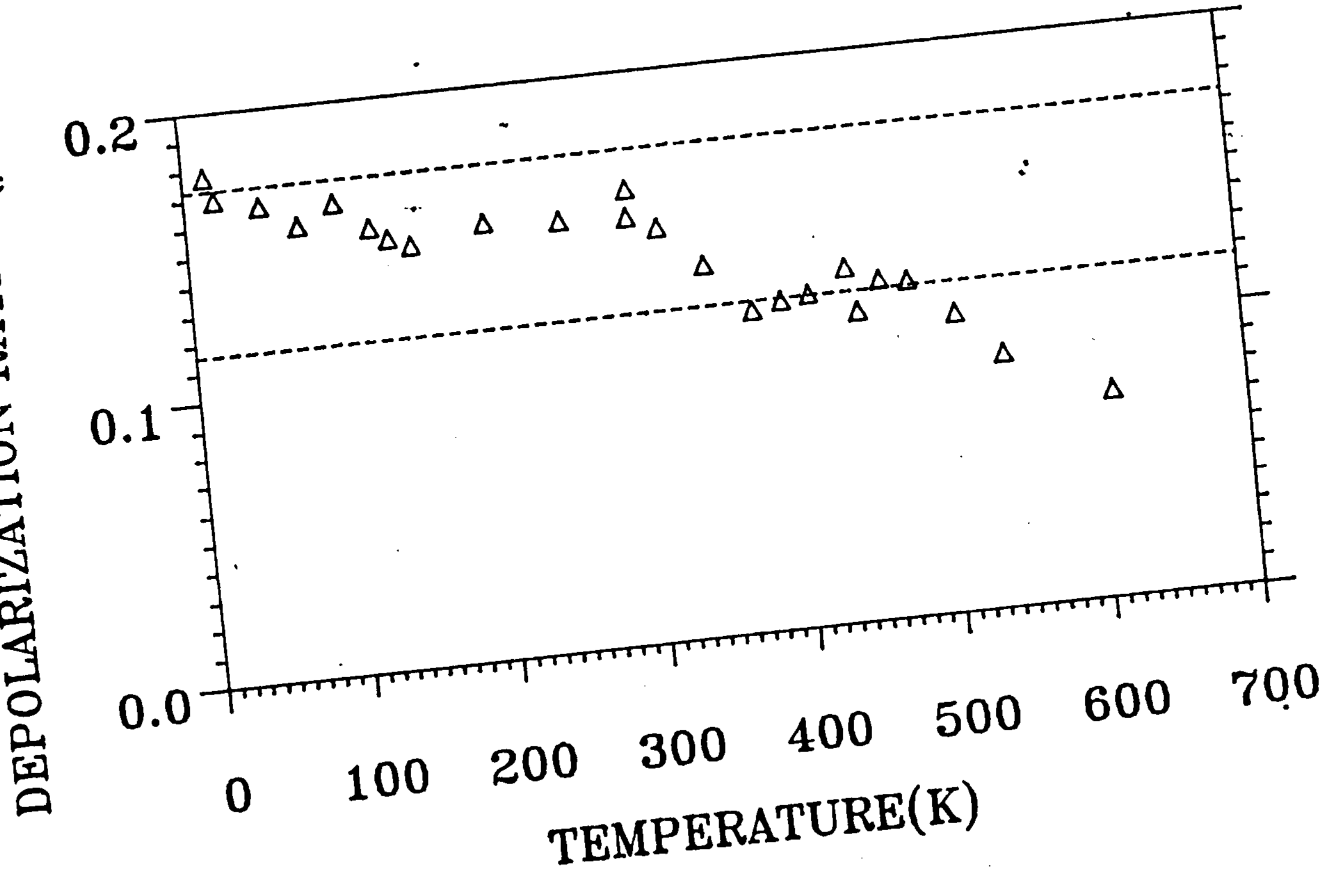
10. W. J. Kossler, H. E. Schone, K. Petzinger, B. Hitti, J. R. Kempton, E. F. W. Seymour, C. E. Stronach, W. F. Lankford and J. J. Reilly, 4th Int. Conf. on Muon Spin Rotation, Uppsala, June 1986, to be published in Hyperfine Interactions.

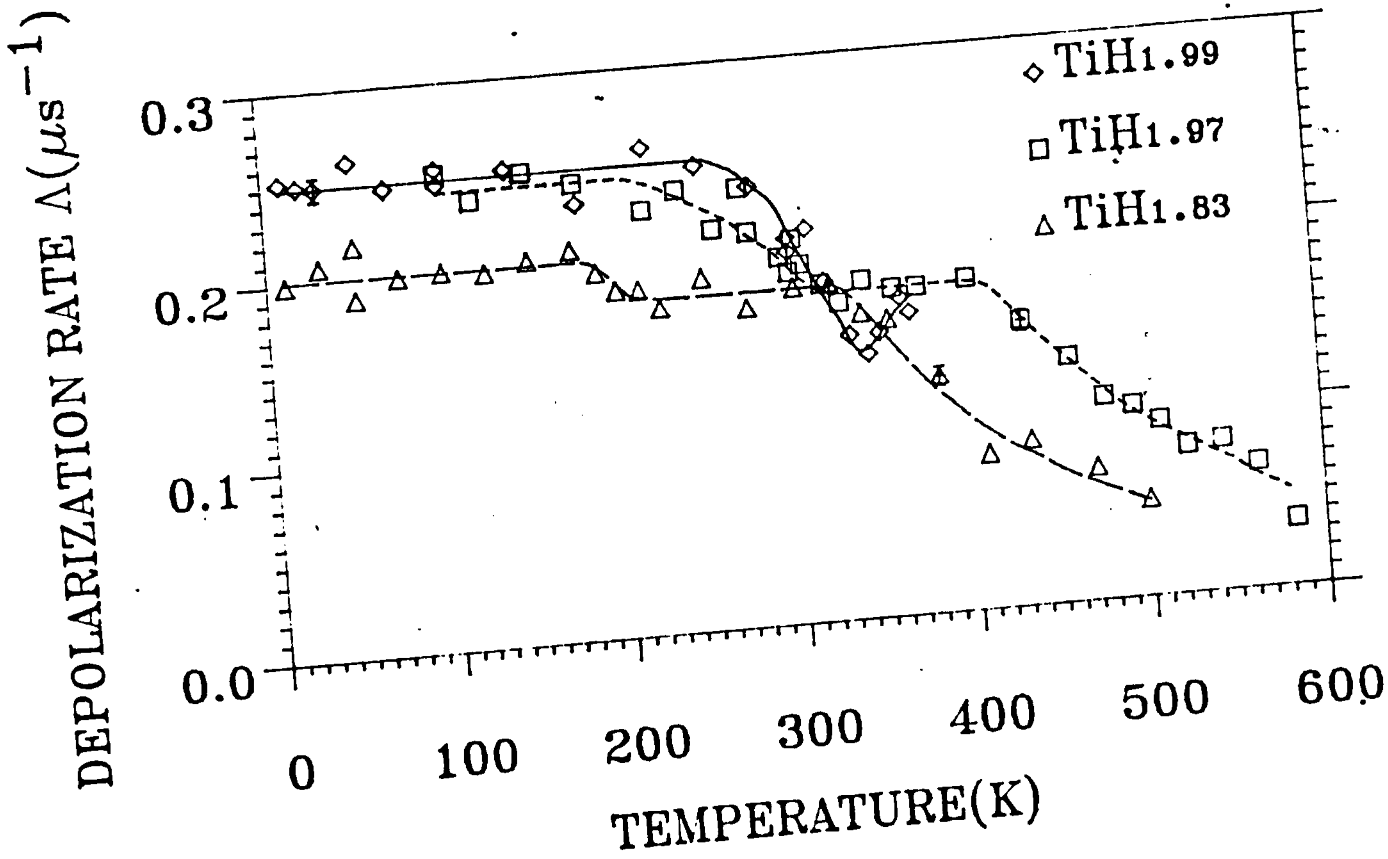


× X=1.83
□ X=1.97
X=1.80
X=1.90
10.0
1.0
0.1
0.01
0.001
Correlation Time (μs)
1.5
2.0
2.5
3.0
1000/T(K)



0.07
0.06
0.05
0.04
0.03
Λ^2
0.00
0.05
0.10
(2−X)/2


0.2
0.1
0.0
0
100
200
300
400
500
600
700
TEMPERATURE(K)
DEPOLARIZATION RATE Λ(μs⁻¹)



TiH1.99
TiH1.97
TiH1.83
DEPOLARIZATION RATE Λ(μs^{-1})
0.3
0.2
0.1
0.0
0
100
200
300
400
500
600
TEMPERATURE(K)